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Title: Electrical Insulating Prepregs and  
Process for Manufacturing Mica Tapes

[Claims]

[Claim 1] An electrical insulating prepreg wherein porous insulating materials or films are coated at ordinary temperature with an epoxy resin composition comprising an epoxy resin that is liquid at ordinary temperature, an ordinary temperature-curing type active curing agent that is liquid at ordinary temperature as first curing agent, and a second curing agent formed of a finely divided latent curing agent that is solid at ordinary temperature, a curing agent microencapsulated, and/or an organic metallic salt curing agent, these agents being used singly or in combination.

[Claim 2] A process for manufacturing a mica tape wherein bonded mica foil is coated and impregnated with a composition prepared by blending an organic metallic salt with an epoxy resin, a backing material side is coated at ordinary temperature with

the epoxy resin composition as described in Claim 1, and thereafter both of these are laminated

[Detailed Description of the Invention]

[0001]

[Industrial Field of Application] This invention relates to a wide variety of prepregs used for the insulation of electrical apparatus and moreover, to a process for manufacturing mica tapes used for the insulation of high-tension rotary apparatus.

[0002]

[Prior Art] Prepregs used hitherto for the insulation of electrical apparatus are manufactured, for example, by the following methods: a method as described in Japanese Patent Laid-Open No. 34639/1990 wherein porous insulating materials such as glass fiber or aramide fiber are coated and impregnated with a solution prepared by dissolving in solvent a known thermosetting resin such as epoxy resin, polyester resin, silicone resin, or polyimide resin and thereafter, the resin undergoes B stage treatment while drying to remove the solvent to finish a prepreg; and a method termed the so-called hot melt method as described in Japanese Patent Laid-Open No. 296542/1992 wherein a base is impregnated with a solvent-free and highly viscous thermosetting resin having been melted to obtain a prepreg.

[0003]

[Problems that the Invention is to solve] In the above-described method to manufacture prepregs by use of solvent, the use of a large amount of solvent not only has an effect on the human body and introduces a problem in environmental pollution but also requires drying facilities and high energy costs, the characteristics of the resulting cured products are deteriorated because thorough removal of the solvent is difficult, and furthermore, the prepregs also have a disadvantage in long-term storage because the resin having undergone the B stage treatment by heating gradually reacts even at low temperature.

[0004] In the hot melt method, the disposal of solvent may bring about improvement in problems such as an effect on the human body, environmental pollution, and the cost for apparatus. However, a compound prepared by melting a highly viscous or hal: solid resin and blending with a curing agent is melted again when the base is impregnated with the compound. Therefore, this method has a disadvantage in that severe process control (temperature, time) is required when melted and that the resin heated once gradually reacts to render long-term storage of prepregs difficult. In addition, the base cannot be impregnated in every nook and corner with the highly viscous resin which introduces a problem in quality.

[0005] The invention has been carried out to solve these

problems and aims to provide a prepreg wherein the base is impregnated with a ~~solvent-free~~ resin at ordinary temperature and in addition, the omission of the heating step and short-term storage make the prepreg tack-free and make a prolonged storage life thereof possible.

[0006] The invention has been done to solve the above-described problems and to develop an epoxy resin composition wherein the viscosity of a resin allows the impregnation of various bases with the resin at ordinary temperature and after impregnating, reaction proceeds in a short period of time to form the prepreg, which in addition, has an extremely long storage life that has never been achieved by former techniques.

[0007]

[Means for Solving the Problems] In the invention of the electrical insulating prepreps relating to claim , the prepreps are manufactured by impregnation of porous insulating materials or films with an epoxy resin composition at ordinary temperature, the composition comprising an epoxy resin that is liquid at ordinary temperature, ~~an ordinary temperature-curing~~ ~~type amine curing agent that is liquid at ordinary temperature,~~ ~~as first curing agent, and a second curing agent formed of a~~ ~~finely divide latent curing agent that is solid at ordinary~~ ~~temperature,~~ a curing agent microencapsulated, and/or an organic metallic salt curing agent, these agents being used

singly or in combination.

[0008] In the invention of the process for manufacturing mica tapes used for high-tension rotary apparatus relating to claim 2, bonded mica foil is coated and impregnated with a composition prepared by mixing an epoxy resin and an organic metallic salt and backing material side is treated with the epoxy resin composition relating to claim 1 at ordinary temperature, and thereafter both of these are laminated, thus to manufacture a mica tape.

[0009]

[Effect] For the epoxy resin composition in the invention of claim 1, bisphenol A, bisphenol F, novolak, and cyclic epoxy resins can be used singly or in combination with one another and in either case, the resins used have an epoxy equivalent of 160 to 300 and are liquid at ordinary temperature.

[0010] The amine curing agents used as first curing agents are modified aliphatic amines, modified alicyclic amines, and modified aromatic amines, all these amines being liquid at ordinary temperature. These curing agents are blended in an amount of 10 to 40 percent to the theoretical amount of the epoxy resins. These epoxy resins and amines react comparatively rapidly at ordinary temperature to achieve a stable B stage state. The presence of two phenomena has been found about this fact. That is, in the reaction between an epoxy resin and a small amount of amine curing agent, one active hydrogen atom of an amido group

(-NH<sub>2</sub>) reacts preferentially and subsequently, another hydrogen atom also gradually reacts to complete gel soon in spite of hydrogen atoms in an amount less than the theoretical amount. As another type, after an active hydrogen atom of an amido group (-NH<sub>2</sub>) reacts preferentially, the residual hydrogen atom does not react any longer at ordinary temperature to form an extremely stable state. In the substances indicating the latter properties, structures having a tendency to induce steric hindrance in molecule are effective. Branched-chain molecules exert a more remarkable action than straight-chain molecules and cyclic molecules containing low-molecular alkyl groups such as methyl group on an aromatic ring exert a more remarkable action than cyclic molecules themselves such as simple benzene ring or cyclic compounds. Thus, use of these curing agents allows easy preparation of tack-free resins. In order to obtain a curing composition excellent in electrical, mechanical and thermal properties, of the amine curing agents, modified alicyclic amines are suitably used and a hydrogenated product of diaminodiphenylmethane or methyl group-substituted cyclic compounds are particularly preferably used.

[0011] When the amount of curing agents used is 10 percent or less to the theoretical amount of the epoxy resin, a rise in viscosity of the resin composition is too small to obtain a desired tack-free resin. On the other hand, exceeding 40 percent may unpreferably promote the reaction of the resin

composition to form gel. Although the amount thereof depends upon a base resin used, it is usually determined in the range of from 20 to 33 percent in consideration of the hardness or flexibility of the prepreg.

[0012] In most of the second curing agents of such resin system, ionic reaction proceeds in catalytic systems as exemplified below. That is, known BF<sub>3</sub> monoethylamine and the derivatives thereof, ~~diacyandiamide~~ hydrazides, and high molecular weight compounds called the amine adducts, and amido group-containing compounds are used, and all these compounds being solid at ordinary temperature. For practical use, it is preferred to pulverize finely the curing agents in order to disperse in the resin.

[0013] Curing agents prepared as microcapsules of a 2 to 5  $\mu$ m size can also be used, wherein highly reactive curing agents such as imidazoles are wrapped in polyvinyl formal, isocyanates, or polycarbonates. The reaction does not start until the shells of the microcapsules are melted and therefore, a stable resin system can be formed by applying to the prepreg and can be very suitably used.

[0014] Furthermore, known organic metallic salts such as zinc octylate, manganese naphthenate, and iron acetylacetonate are suitably used, which hardly react with the epoxy resins at ordinary temperature but present curing and catalytic actions at high temperature.

[015] It is a matter of course that these curing agents can be used simply or in combination, depending upon desired characteristics of cured products.

[016] When two curing agents are mixed with the epoxy resin, a higher reactive curing agent first reacts and a lower reactive (slower) curing agent is left in the reaction system. As a result, an unreacted curing agent is left resulting in forming cured products inferior in electrical, mechanical, and thermal characteristics. In the epoxy resin composition according to the invention, the synergistic effect by the first and the second curing agents forms cured products excellent in various characteristics particularly by the effect of ionic reaction in the second reaction and hydrogen loss in molecule, as compared with the respective systems prepared by mixing separately the curing agents with the epoxy resin. The present inventor has confirmed this and accomplished this invention.

[017] The above-described epoxy resin composition of the invention can be used for the preparation of a dry type bonded mica tape having the following characteristics because a prepreg having a desired viscosity can be easily prepared by changing the content of the first curing agent.

[018] Bonded mica foil is coated and impregnated with the epoxy resin composition prepared by mixing an organic metal salt with a known epoxy resin in solvent type, and then dried. The backing material side is coated and impregnated,



for example, with an imidazole microencapsulated, which is highly effective in promoting reaction with an impregnating resin, as the second curing agent in solvent-free type to laminate with the bonded mica, thus a mica tape being obtained. This mica tape is wound onto an insulating coil for a high-tension rotary apparatus, heated under vacuum, impregnated with an impregnating resin prepared by adding an acid anhydride curing agent and furthermore a reactive diluent such as styrene to an epoxy resin widely used as an impregnating resin, cured by heating to obtain an insulating coil. That is, imidazoles highly effective in promoting reaction with the above-described impregnating resin react easily with the epoxy resin and therefore, cannot be usually used for the mica tape that requires a high tape life. When used inevitably, a resin such as polyester resin that hardly reacts with imidazoles is selected as a base resin. However, mixing with polyester resin inferior in characteristics such as heat resistance and adhesion after impregnating and curing, as compared with the above-described epoxy impregnating resin, results in deterioration in qualities of insulating coils and consequently, the practical use thereof is avoided. Since microcapsules that form shells for the imidazoles are easily dissolved in usual solvents, a resin system containing styrene in the impregnating resin initiates reaction even at ordinary temperature when impregnated with the resin and therefore, the reaction promoting effect is further

accelerated, which exerts a great effect to simplify the insulating treatment.

[0019] In the invention, in addition to the imidazoles, the second curing agents can be selected and used in consideration of a curing-promoting effect in connection with impregnating resins used.

[0020]

[Examples]

Example 1: One hundred parts of Epicoat 828 (Epoxy Equivalent: 190 grams/eq., Yuka Shell-sha) as bisphenol A type epoxy resin, 10 parts of Epicure-113 (A hydrogenated ~~4,4'-diaminodiphenylmethane~~ derivative, Viscosity: 125 cps/25°C, Yuka Shell-sha) as the first curing agent, and 20 parts of Novacure-HX3722 (Microcapsule type ~~imidazole~~, pasty state, Asahi Chemical Industry Co., Ltd.) as the second curing agent were mixed at ordinary temperature. This mixture was coated onto glass cloth of a 0.3 thickness (Arisawa Seisakusho) at ordinary temperature so as to be 50 percent in resin content and stored at 30°C. ~~After~~ 24 hours, a tack-free prepreg was obtained.

[0021] Example 2: One hundred parts of Epicoat 807 (Epoxy equivalent: 167 grams/eq. Yuka Shell-sha) as Bisphenol F type epoxy resin, 11 parts of Epicure-113 (described above) as the first curing agent, and 20 parts of Novacure-HX3722 (described above) as the second curing agent were mixed at ordinary

temperature. The mixture was coated onto the glass cloth of a 0.18 thickness (described above) at ordinary temperature so as to be 50 percent in resin content and stored at 30°C. After 24 hours, a tack-free prepreg was obtained.

[0022] Example 3: Fifty parts of Epicoat 828 (described above), 50 parts of Epicoat 152 (epoxy Equivalent: 175 grams/eq., Yuka Shell-sha) as novolak type epoxy resin, 11 parts of Epicure-113 (described above) as the first curing agent, and 20 parts of Novacure-HX3722 (described above) as the second curing agent were mixed at ordinary temperature. The mixture was coated on the glass cloth of a 0.18 thickness (described above) at ordinary temperature so as to be 50 percent in resin content and stored at 30°C. After 24 hours, a tack-free prepreg was obtained.

[0023] Example 4: One hundred parts of Epicoat 828 (described above), 11 parts of Epicure-3080 (Modified aliphatic amine, Viscosity: 8.0 cps/25°C, Yuka Shell-sha) as the first curing agent, and 20 parts of Novacure-HX3722 (described above) as the second curing agent were mixed at ordinary temperature. The mixture was coated onto the glass cloth of a 0.18 thickness (described above) at ordinary temperature so as to be 50 percent in resin content and stored at 30°C. After 24 hours, a tack-free prepreg was obtained.

[0024] Example 5: Fifty parts of Epicoat 828 (described above), 50 parts of Epicoat 152 (described above) as Novolak

type epoxy resin, 11 parts of Epicure-113 (described above) as the first curing agent, 6 parts of finely divided dicyandiamide (Yuka Shell-sha) as the second curing agent, and 4 parts of Novacure-BX3722 (described above) as catalyst were mixed at ordinary temperature. The mixture was coated onto the glass cloth of a 0.18 thickness (described above) at ordinary temperature so as to be 50 percent in resin content and stored at 30°C. After 24 hours, a tack-free prepreg was obtained.

[0025] Comparative Example 1: Sixty parts of methyl ethyl ketone was added to 40 parts of Epicoat 834 (Epoxy equivalent: 250 grams/eq., Yuka Shell-sha) as bisphenol A type epoxy resin and 60 parts of Epicoat 1001 (Epoxy equivalent: 475 grams/eq., Yuka Shell-sha) and dissolved. A solution prepared beforehand by dissolving 6 parts of dicyandiamide (described above) as curing agent and 0.3 part of 3,4-dichlorophenyl-1,1-dimethylurea (Yuka Shell-sha) in 30 parts of methyl cellosolve was mixed with the above-described solution to prepare a varnish. This varnish was coated onto the glass cloth of a 0.18 thickness (described above) at ordinary temperature so as to be 50 percent in resin content and dried at 100 to 135°C for 7 minutes to obtain a tack-free prepreg (Content of remaining solvent: 0.2 percent).

[0026] Comparative Example 2: Twenty-five parts of Epicoat 834 (described above) and 75 parts of Epicoat 1001 (described above) as epoxy resins were mixed at 65°C. Thirty

parts of Novacure-HX3722 (described above) as curing agent was added to the mixture and rapidly kneaded at the same temperature. This was coated onto the glass cloth of a 0.3 thickness (described above) at 65°C to 75°C so as to be 50 percent in resin content to obtain a tack-free prepreg. However, too high viscosity thereof resulted in extremely deteriorating the coating operating properties thereof and in addition, caused much unevenness in coating.

[0027] In order to confirm the effect of the invention, the storage life of the prepreps obtained in Examples and Comparative Examples at 30°C was indicated as times (days) passing until the prepreps gel. Five prepreps were superposed, and molded at 150°C for 5 hours to obtain a laminated sheet of a 1.0 thickness. The finished state and the glass transition temperatures ( $T_g$ ) of the laminated sheets determined by heat penetration method are shown in Fig. 1. The prepreps of the invention were found excellent in all characteristics as compared with prepreps known hitherto.

[0028] Example 6: This example relates to a process for manufacturing mica tapes. Forty parts of Epicoat 834 (described above) and 60 parts of Epicoat 1001 (described above) as the epoxy resins were added to and dissolved in 10 parts of zinc octylate as curing agent and 160 parts of ethyl ethyl ketone to prepare a varnish. The varnish was coated onto bonded mica foil of a 0.10 thickness (non-burning type DR- Okabe Mica

Kogyosho) so as to be 5 percent in resin content and dried at 80°C to 120°C for minutes. As a backing material for the mica foil, a composition kneaded at ordinary temperature which comprised 100 parts of Epicoat 828 (described above), 10 parts of Epicure-113 (described above) as the first curing agent, and 10 parts of zinc octylate and 10 parts of Novacure-HX722 (described above) as the second curing agents was coated onto glass cloth of a .03 thickness (Arisawa Seisakusho) so as to be 15 percent in resin content. This was superposed on the prepreg treated mica foil, and passed between heated rolls adjusted to 50°C to laminate, thus a mica tape having a 0.135 thickness and a resin content of 7.5 percent being prepared.

[0029] This mica tape was wound ten times on a coil conductor of a 1-meter length where flat type double layer glass covered wire of 2.0 x 7.0 in thickness (Mitsubishi Cable Industries, Ltd.) was formed into a two row-twenty stage structure. After a glass tape of a 0.13 thickness was wound once for the protection of the mica tape, the coil conductor was heated under vacuum, impregnated with a styrene-modified epoxy impregnation resin containing, as principal constituents, a bisphenol A type epoxy resin, an acid anhydride curing agent, and a styrene monomer (DR311, Ryoden Kasei), and then heated at 135°C for 24 hours to obtain an insulating coil. Tan  $\delta$  (2KV value) and ATan  $\delta$  (5 KV-2 KV value) of the insulating coil were 0.58 percent and 0.10 percent, respectively, and very

satisfactory.

[0030] Comparative Example 3: Forty parts of Epicoat 834 (Epoxy equivalent: 250 grams/eq., Yuka Shell-sha) and 60 parts of Epicoat 1001 (Epoxy equivalent: 475 grams/eq., Yuka Shell-sha) as epoxy resins were added to and dissolved in ten parts of zinc octylate as curing agent and 160 parts of methyl ethyl ketone to prepare a varnish. The varnish was coated on bonded mica foil of a 0.10 thickness (non-burning type DR-2, Okabe Mica Kogyosho) so as to be five percent in resin content, and dried at 80°C to 120°C for 7 minutes. As the backing material for the mica foil, the above-described epoxy composition was coated onto the glass cloth of a 0.03 thickness (described above), and dried at 80°C to 120°C for 7 minutes so as to be 15 percent in resin content. This was superposed on the prepreg on the above-described mica foil and passed between heated rolls maintained at 50°C to laminate, thus a mica tape having a 0.135 thickness and a resin content of 7.5 percent being prepared.

[0031] The mica tape was wound ten times on a coil conductor of a 1.0 meter where flat type double fiber glass covered wire of a 2.0 x 7.0 thickness (described above) is formed into a two row-twenty stage structure. After a glass tape of a 0.13 thickness was wound once for the protection of the mica tape, the coil conductor was heated under vacuum, impregnated with the styrene modified epoxy impregnating resin (described above), and then heated at 135°C for 24 hours to obtain an

insulating coil.  $\tan \delta$  (2 KV value) :  $\Delta \tan \delta$  (15 KV-2 KV value)  
of the insulating coil were 0.78 percent and 1.50 percent,  
respectively.

[0032]

[Advantage of the Invention] The electrical insulating  
prepregs of the invention form tack-free prepregs simply by  
coating base materials without requiring organic solvent and  
heat drying stage. Consequently, the manufacturing stages  
present no effect on the human body and no problem in  
environmental pollution and furthermore, require no drying  
facilities and no energy costs. In addition, the prepregs have  
the advantages of having a high storage life, rapidly curing  
by heat when used, and giving cured products excellent in  
electrical, mechanical, and thermal properties.

[0033] In the insulating coil prepared according to the  
process for manufacturing a mica tape of the invention, the  
prepreg composition that has a large reaction promoting effect  
on the impregnating resin is contained in the backing material  
side. Therefore, in the heating after impregnating by heating  
under vacuum, the viscosity of the impregnating resin decreases  
and simultaneously, curing reaction proceeds without leakage  
of resin in the insulating layer. As a result, bubbles hardly  
develop and a good insulating coil is obtained.

The storage lives, appearance of the products and glass  
transition temperatures ( $T_g$ ) of Examples and Comparative



Examples in the invention are shown in Table 1.

Table 1]

	Example					Comparative Example	
	1	2	3	4	5	1	2
Storage life (days)	90 or more	90 or more	90 or more	90 or more	90 or more	40	60
Appearance after formation	Good	Good	Good	Good	Good	Some Bubbles	Uneven
T <sub>g</sub> (°C)	168	162	170	160	158	134	142